ADHESIVE BONDING OF CARBON FIBER REINFORCED PLASTIC TO ADVANCED HIGH STRENGTH STEEL

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Co-PI: Kevin Simmons, Pacific Northwest National Laboratory

2019 DOE VTO Annual Merit Review

June 12, 2019

Project ID # MAT-137

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OVERVIEW

Timeline

- Start: Oct, 2017
- Finish: Sept, 2020
- 50% Complete

Budget

- Project Funding – $1.867M
  - FY18 - $667K
  - FY19 - $600K

Barriers*

- Limited scientific understanding of joining mechanisms for metal to composite joints
- Few technologies exist for joining metals to composites
  - Low joint strength
  - Crack arrest resistance in crash
  - Thermal expansion mismatch
  - Durability and environmental effects

*2017 U.S. DRIVE Roadmap Report, Section 5

Partners

- Oak Ridge National Laboratory
- Pacific Northwest National Laboratory

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RELEVANCE

- **EERE-VTO Goal:**
  - By 2025, demonstrate a cost-effective 25% weight reduction in passenger vehicles compared to 2010 model (2017 U.S. DRIVE Roadmap Report, Section 5)
- **Project Objectives**
  - Early-stage R&D focusing on
    - Fundamental understanding of CFRP to AHSS adhesive bonding characteristics at nano/micro scales;
    - Identify and explore innovative adhesive bonding concepts and approaches for performance and productivity through scientific understanding
    - Develop better tools for adhesive bonding performance, joint design, and lifetime prediction
    - Closely interact with the **Interface by Design** Task
  - Enable increased use of CFRP in multi-material body structure for weight reduction

FY19 MILESTONES

Milestone Name/Description	End Date	Type
Demonstrate completion of surface characterization of PP and Nylon CFRP and DP980 steel to determine the surface chemistry and surface morphology	12/30/2018 Completed	Quarterly Progress Measure (Regular)
Determine the contribution of variation in surface chemistry and roughness on strength and performance of CFPC to steel adhesive joint	9/30/2019	Quarterly Progress Measure (Regular)

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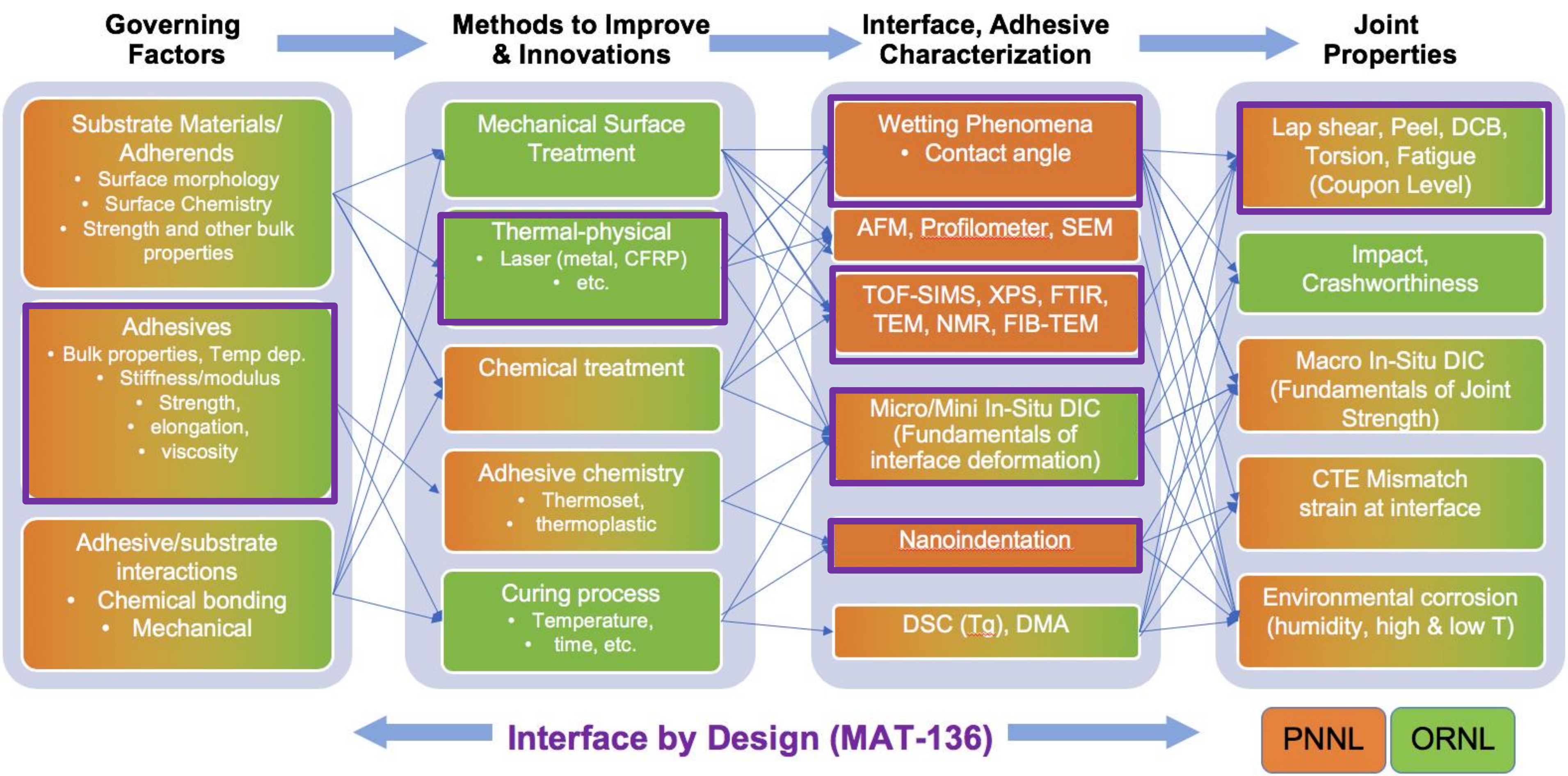
APPROACH

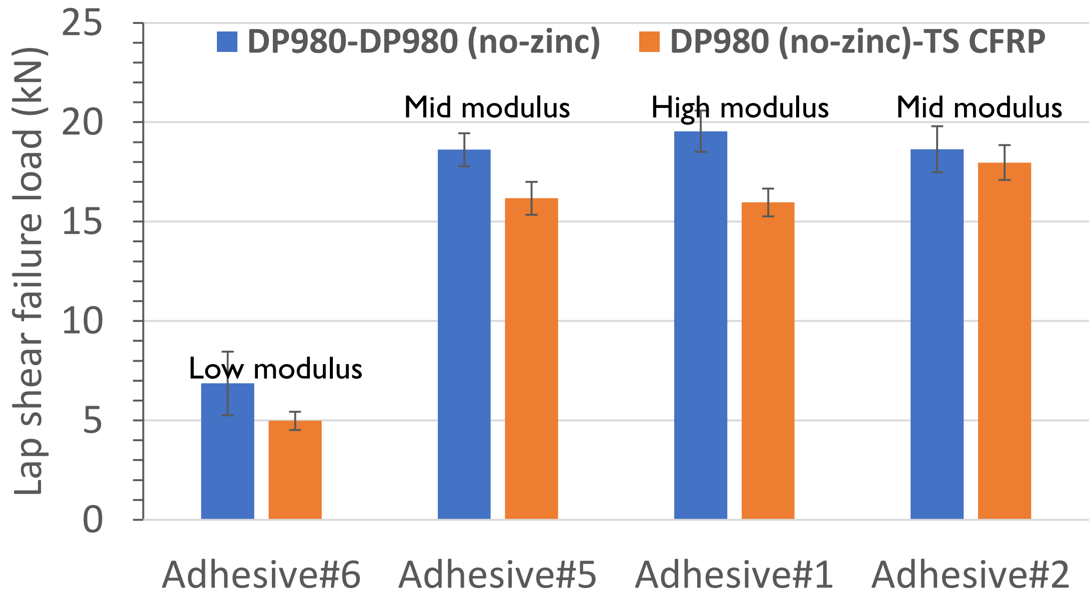
OVERALL PLAN FOR ADHESIVE BONDING OF CFRP-AHSS



FY19 Focus

ACCOMPLISHMENTS AND PROGRESS

MECHANICAL TESTING-LAP SHEAR TENSILE



- No surface treatment on adherends (thermoset CFRP, DP980)
- Lap shear failure load is increased as increased modulus of adhesive
- Lap shear failure load for DP980-DP980 case is higher than the DP980-CFRP for single lap shear testing
- All samples showed cohesive failure mode

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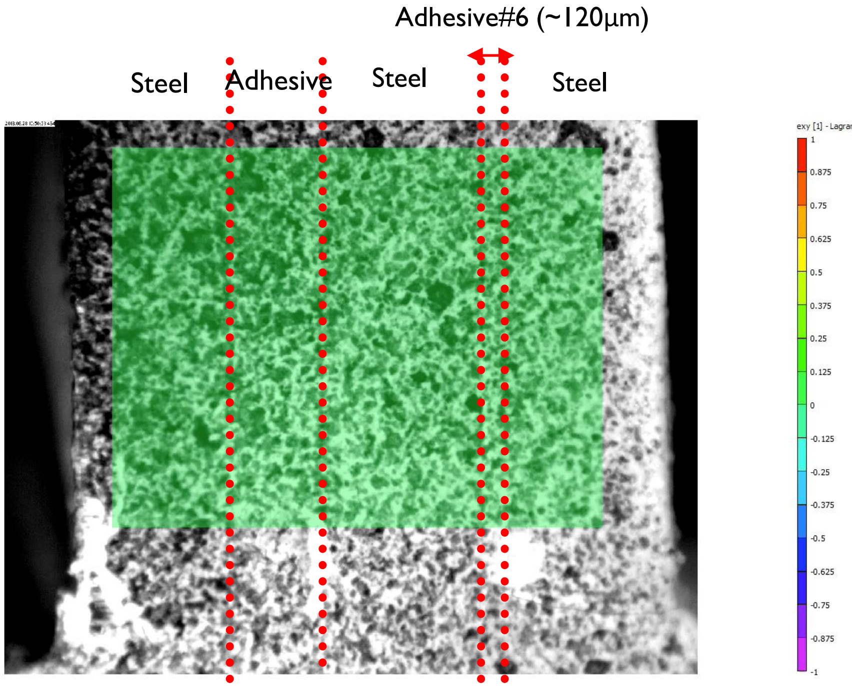
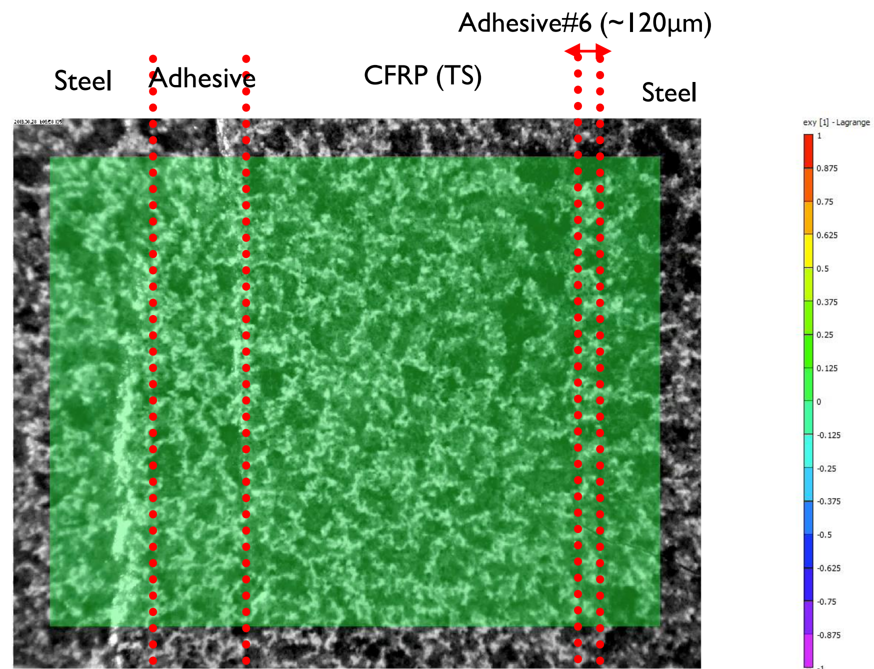
ACCOMPLISHMENTS AND PROGRESS
MICRO DIGITAL IMAGE CORRELATION



Double lap shear (DP980-DP980-DP980)

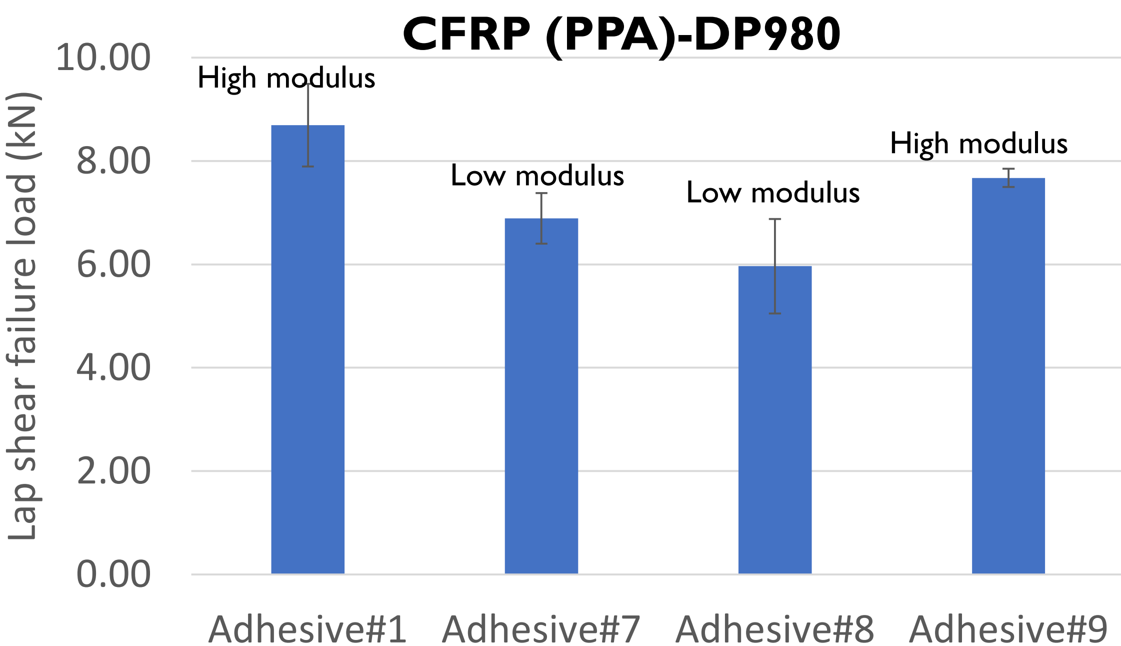


Double lap shear (DP980-CFRP(TS)-DP980)

Sample	Peak strain in adhesive at failure (left)	Peak strain in adhesive at failure (right)	Peak shear failure load (kN)
DP980-DP980-DP980	-0.261	0.448	13.68
DP980-CFRP(TS)-DP980	-0.338	0.945	11.97

Pa

MECHANICAL TESTING-LAP SHEAR TENSILE



- No surface treatment on adherends (CFRP(PPA), DP980)
- Relatively low lap shear strength of CFRP(PPA)-DP980, compared to CFRP (TS)-DP980 case
- Most of samples showed **adhesive failure interface between CFRP (PPA) and adhesive**
- ***Need to engineer adherend surface to improve bonding strength***

- Adhesive#1: Bare DP980: t=1.2mm; CFRP (PPA): t=3.0mm; Curing: supplier recommendations
- Adhesive#7,8,9: Bare DP980: t=1.0mm; CFRP (PPA): t=3.0mm; Curing: supplier recommendations

Adhesive#1

Adhesive#7

CFRP (PPA) DP980 (bare)

Adhesive#8

CFRP (PPA) DP980 (bare)

Adhesive#9

CFRP (PPA) DP980 (bare)

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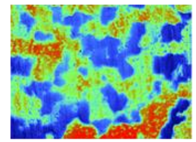
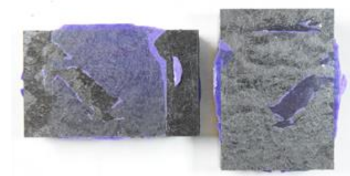
INVESTIGATING THE RELATIONSHIP BETWEEN SURFACES AND ADHESIVES

Surface Analysis
- Morphological
- Chemical
- Physical

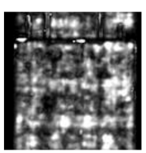


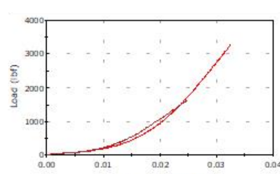


Mechanical testing

Fracture Analysis
- Morphological
- Chemical

Bond NDE
- Acoustic analysis





$\sigma = f$ (surface, adhesive, defect)

Corelate
- Adherend surface
- Strength of adhesive
- Defects measured by NDE
- Fractures

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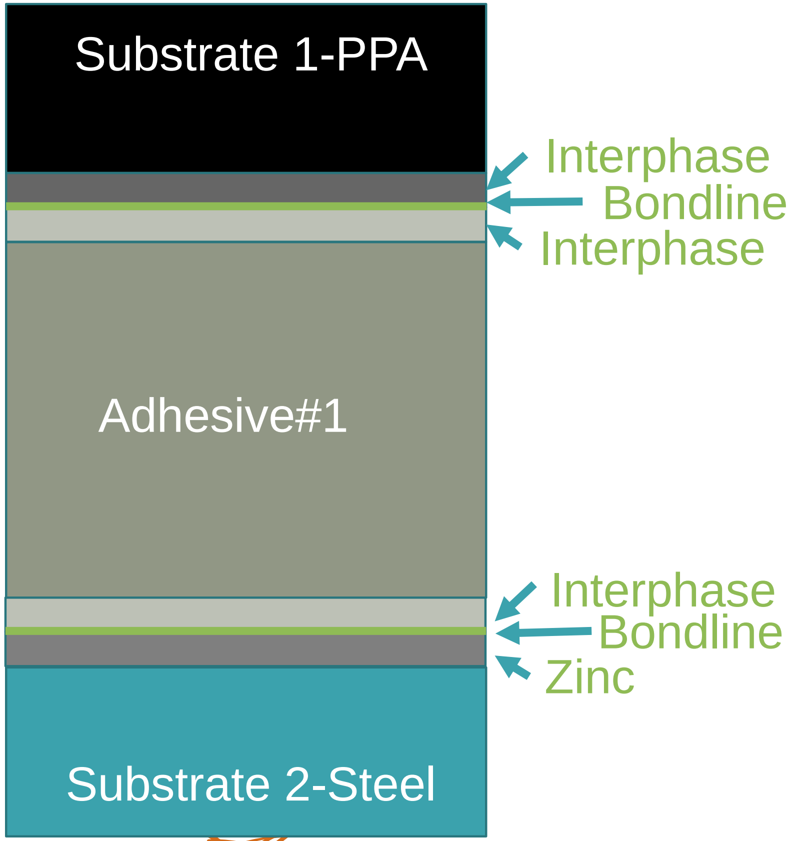
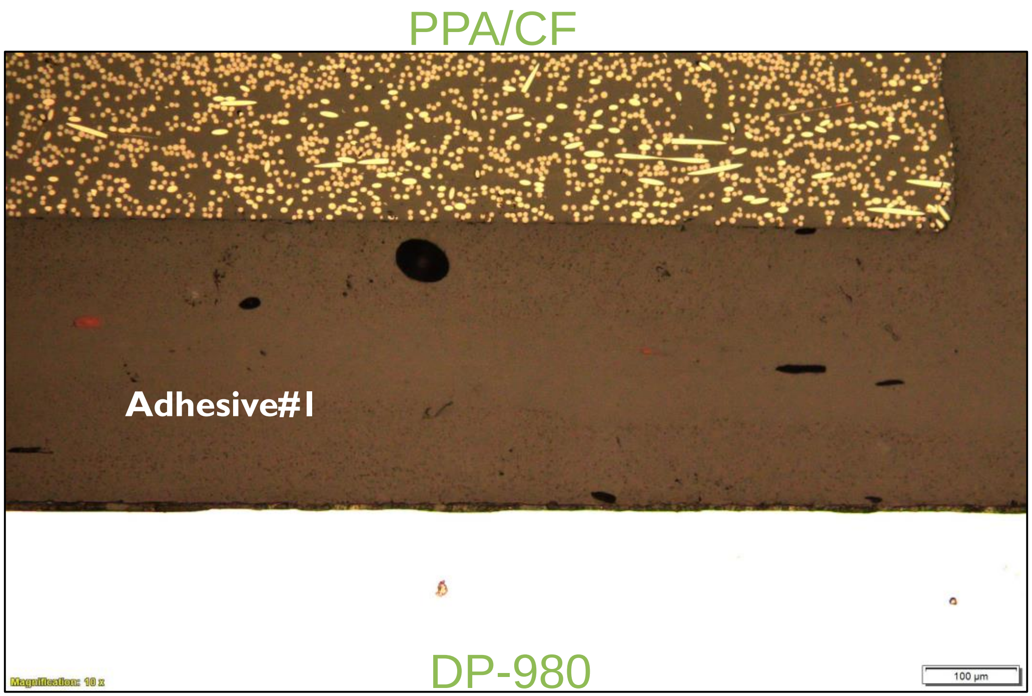
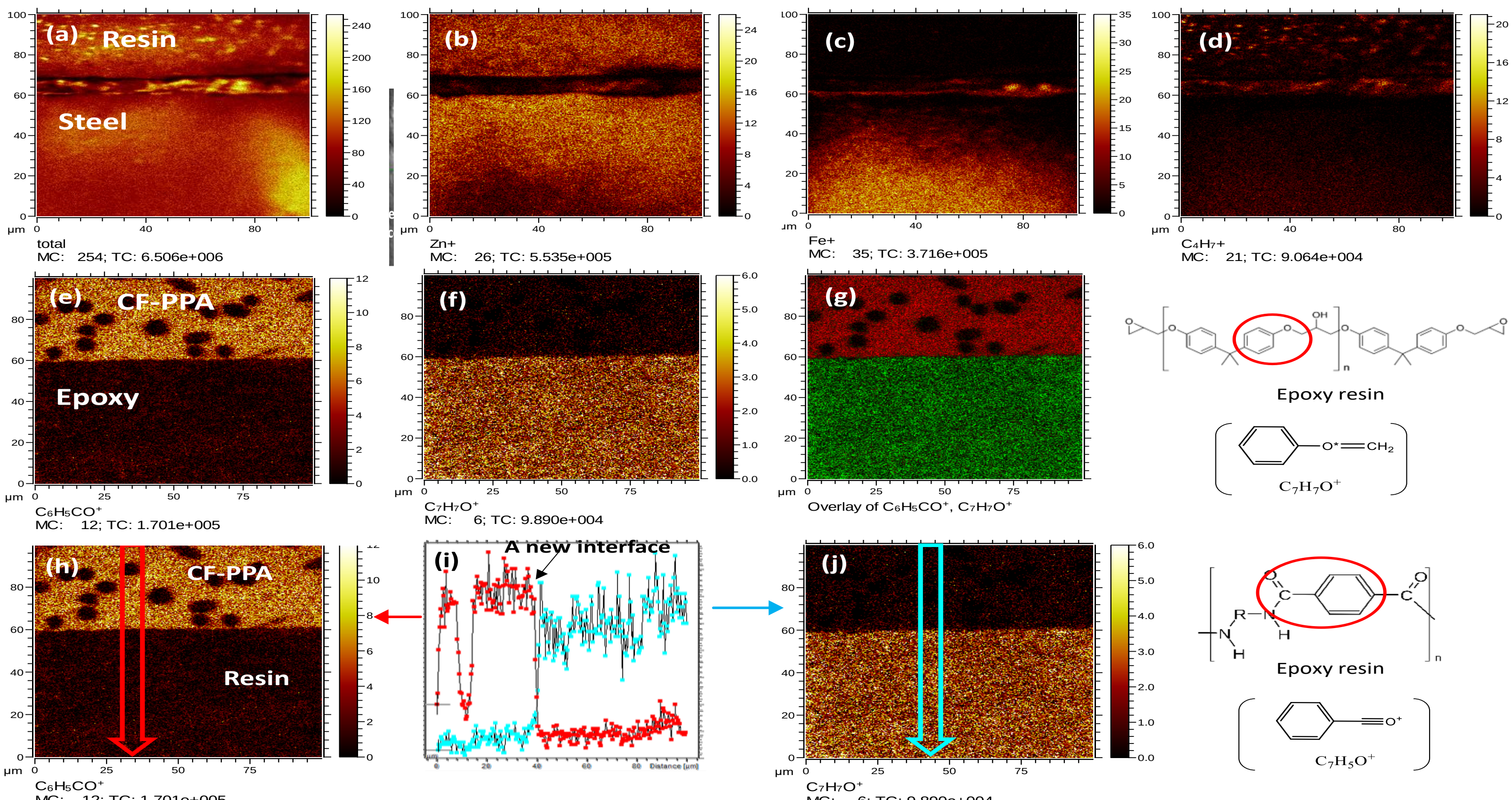
INTERFACIAL BOND LINE CHARACTERIZATION - INTERPHASE

Schematic of Interphases





ACCOMPLISHMENTS AND PROGRESS
INTERFACIAL CHEMICAL BOND LINE ANALYSIS



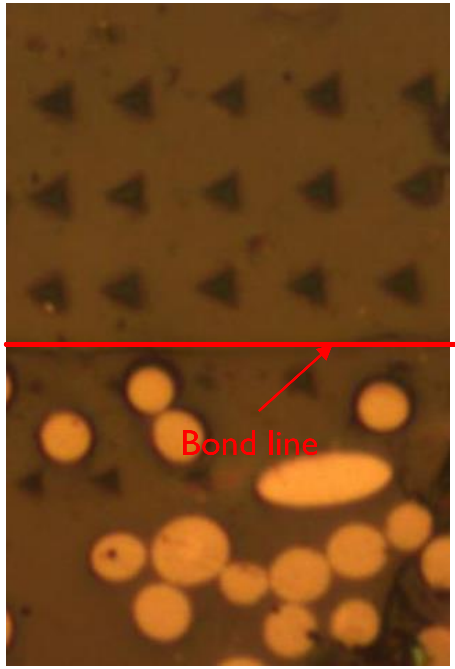
(i)TOF-SIMS indicate adhesive interphase development from adhesive bulk to material #1 bulk through the interface

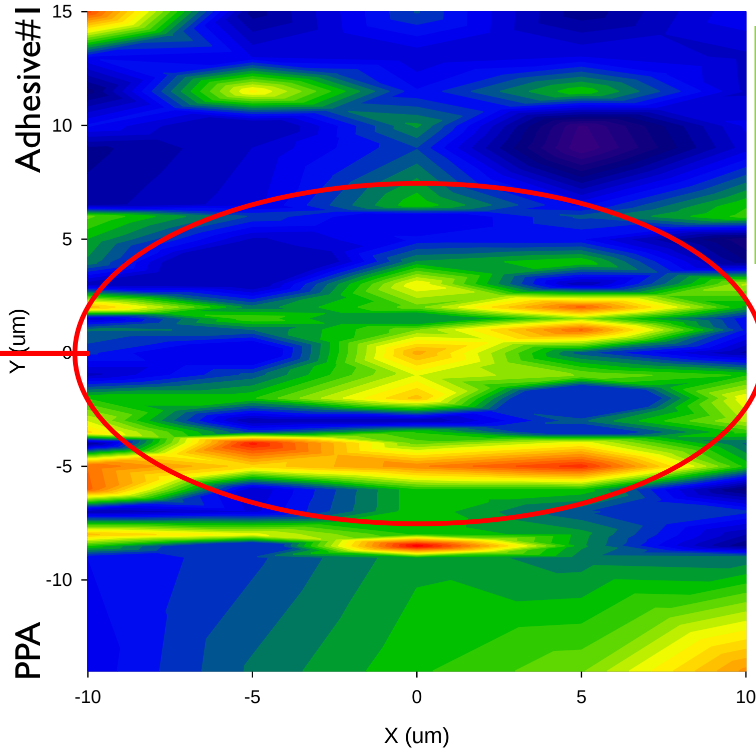
BOND LINE NANOINDENTATION – ADHESIVE #1 TRANSITION TO MATERIAL #1

Representative indents

Merged contour map (6 5X5 matrices)

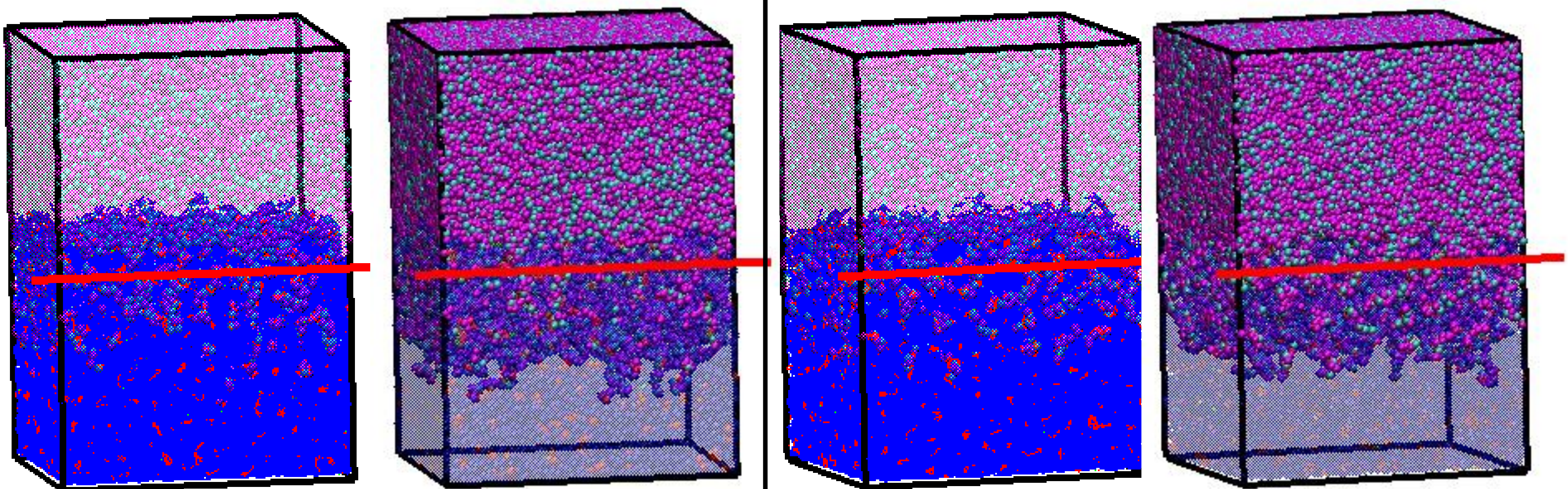
Adhesive #1
Interphase
Interface
Interphase
Material #1





Improved mechanical performance between bond line and 10 um into PPA, consistent to previous data

MOLECULAR DYNAMIC SIMULATION OF INTERFACIAL PROPERTIES INSIDE TWO REGIONS



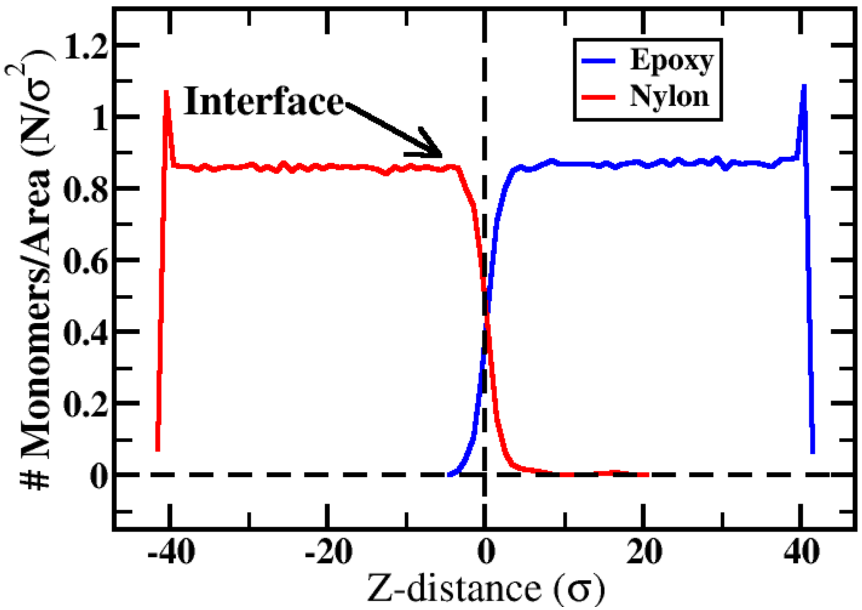
Magenta and Cyan: Nylon nonpolar and polar monomers
Blue and Torquoise: Epoxy nonpolar and bond-forming polar monomers

SCHEME 1: Epoxy and Nylon do not interact with each other during crosslinking.
Nylon diffuse in larger numbers in Epoxy Domain.

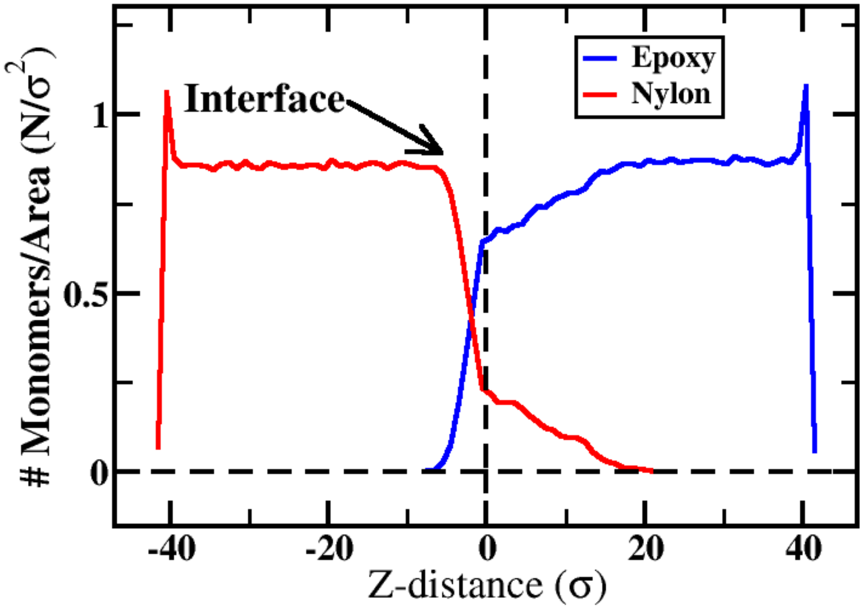
SCHEME 2: Epoxy and Nylon interact favorable (attractive) during crosslinking.
Also, large amount of Nylon in Epoxy Domain.

Both side figures: Both nylon and epoxy phase color made transparent to visualize migration of one into the other

DIFFUSION PROFILE



SCHEME 1: Nylon diffuse in Epoxy layer with a steep gradient but penetration is low

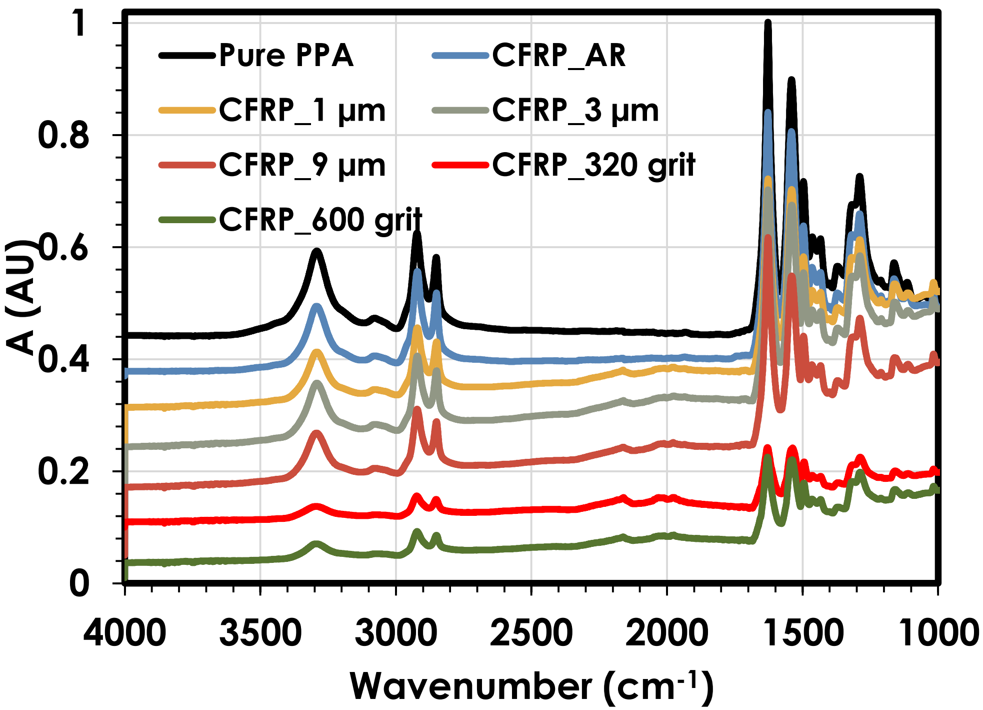


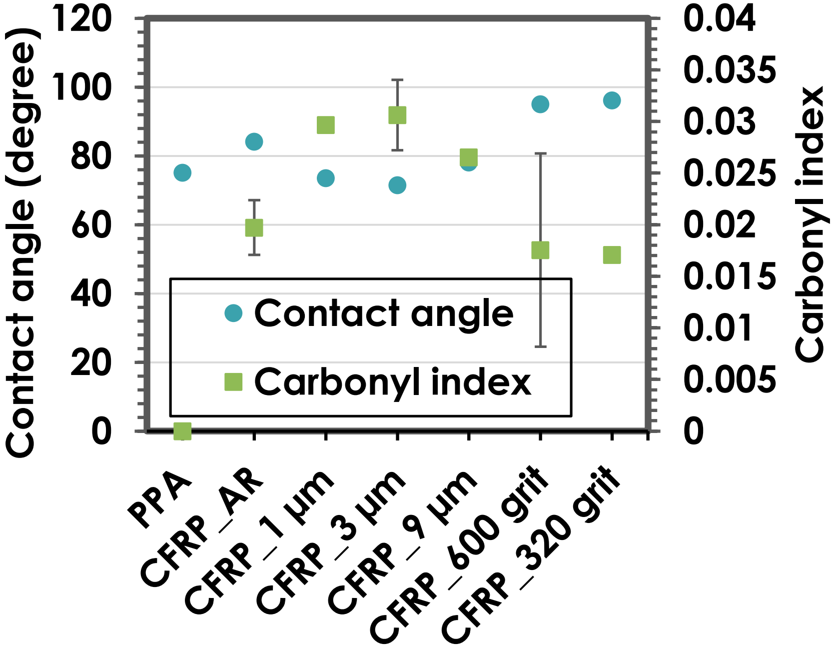
SCHEME 2: Large amount of Nylon in Epoxy layer. The gradient is shallow and penetration is high.

TOF-SIMS and nanoindentation experimentally indicate changes at the interface supporting MD results

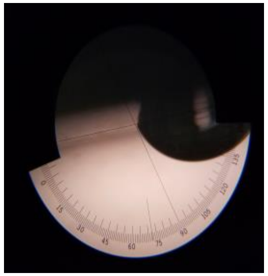
SURFACE ENERGY/CONTACT ANGLE CHARACTERIZATION

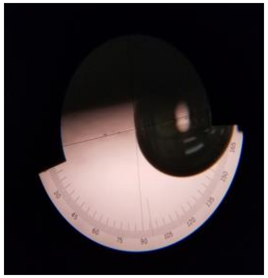
Surface modification: mechanical abrasion





Pure PPA no oxidized peak at 1740cm^{-1} observed
Mechanical abrasion influences contact angle and surface chemistry





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SURFACE ENERGY CHARACTERIZATION CRFP-PPA

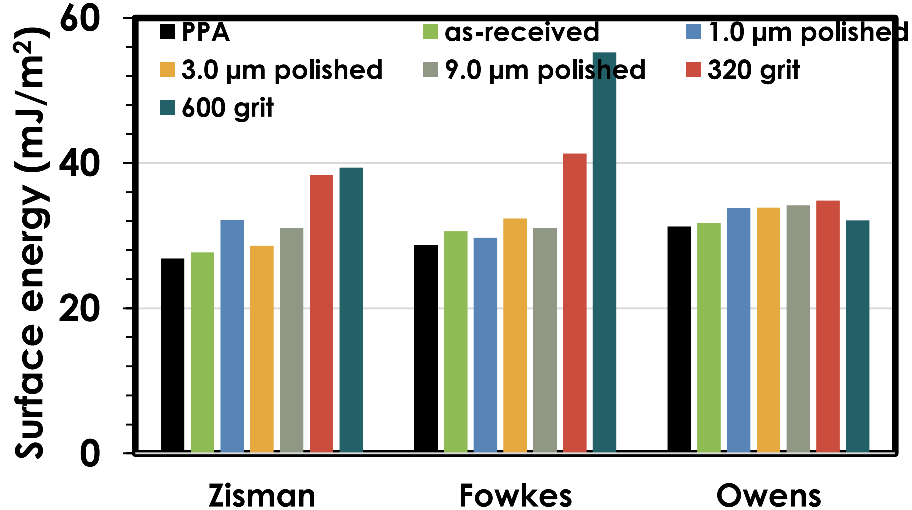
Surface modification: mechanical abrasion

Calculated Surface energies of CFRP-PPA (mJ/m²)

	Zisman ($\gamma_s = \gamma_{cr}$)	Fowkes (γ_s)	Fowkes γ_s^p	Fowkes γ_s^d	Owens-Wendt (γ_s)	Owens-Wendt γ_s^p	Owens-Wendt γ_s^d
PPA	26.9	28.7	*18.5*	*10.3*	31.3	*16.7*	*14.6*
CFRP_AR	27.7	30.6	*6.8*	*23.8*	31.8	*7.5*	*24.2*
CFRP_1 µm	32.1	29.8	*10.3*	*19.5*	33.8	*7.8*	*26.0*
CFRP_3 µm	28.6	32.4	*16.26*	*16.1*	33.9	*17.4*	*16.5*
CFRP_9 µm	31.1	31.1	*11.1*	*20.0*	34.2	*11.3*	*22.9*
CFRP_600 grit	39.4	55.2	*0.1*	*55.1*	32.2	*15.3*	*16.8*
CFRP_320 grit	38.4	41.3	*2.7*	*38.6*	34.8	*11.1*	*23.7*

Surface roughness through mechanical abrasion exposes CF influencing surface energy

Surface energy (γ_s)



Roughness factor

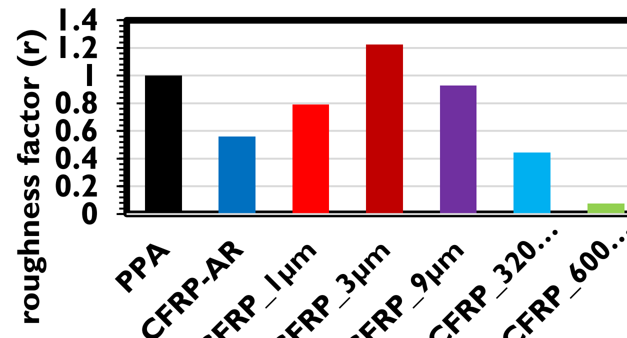
Wenzel equation

$$\cos\theta_w = r\cos\theta_0$$

r: roughness factor

θ_w: equilibrium contact angle

θ_0: intrinsic contact angle



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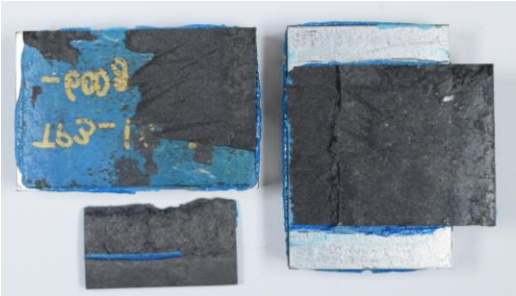
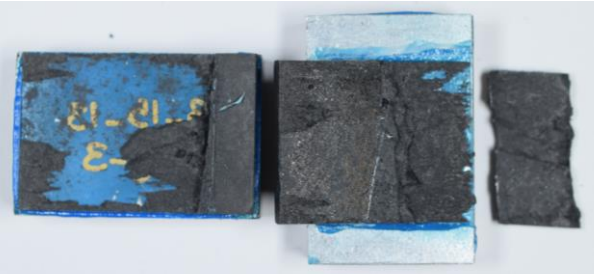
MECHANICAL TESTING-CROSS TENSION

Surface modification: mechanical abrasion

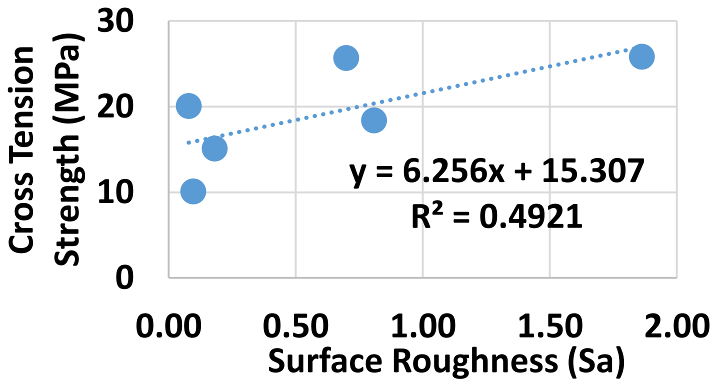
TP3 8-4 As Received TP3-8-13 3 µm polished



600 grit



320 grit



Mechanical abrasion influence on cross tension testing

Surface Treatment	Roughness, Sa (µm)	Roughness, Sz (µm)	X-tension Strength (MPa)
As Received	0.808 ± 0.289	46.927 ± 7.308	18.39
1µ polish	0.09 ± 0,015	6.483 ± 2.338	15.11
3µ polish	0.097 ± 0.014	3.306 ± 1.222	10.1
9µ polish	0.182 ± 0.034	24.411 ± 6.212	20.05
600 grit	0.699 ± 0.053	28.597 ± 2.229	25.81
320 grit	1.862 ± 0.406	37.563 ± 1.200	25.66

All lap shear DP980/PPA-40% specimens tensile failed on the PPA adherend. Bending stresses influenced strength

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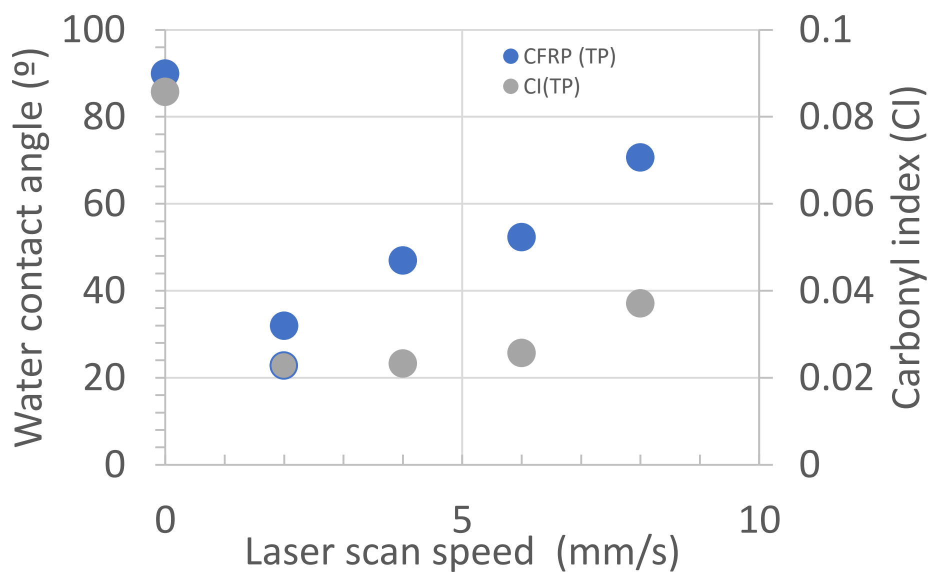
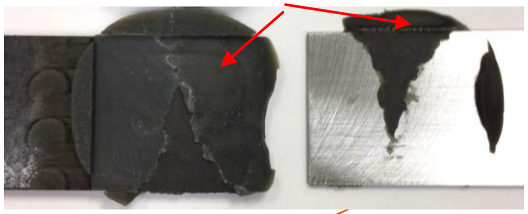
LASER TREATMENT ON CFRP(PPA) SURFACE

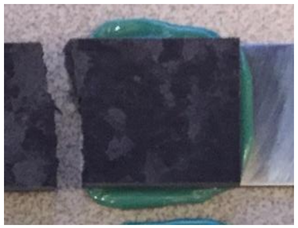
Surface modification: laser treatment



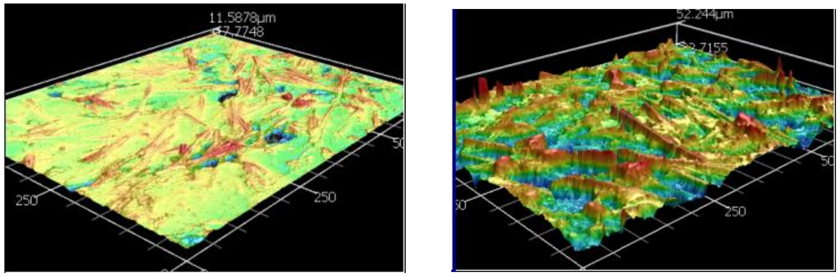
Adhesive#7



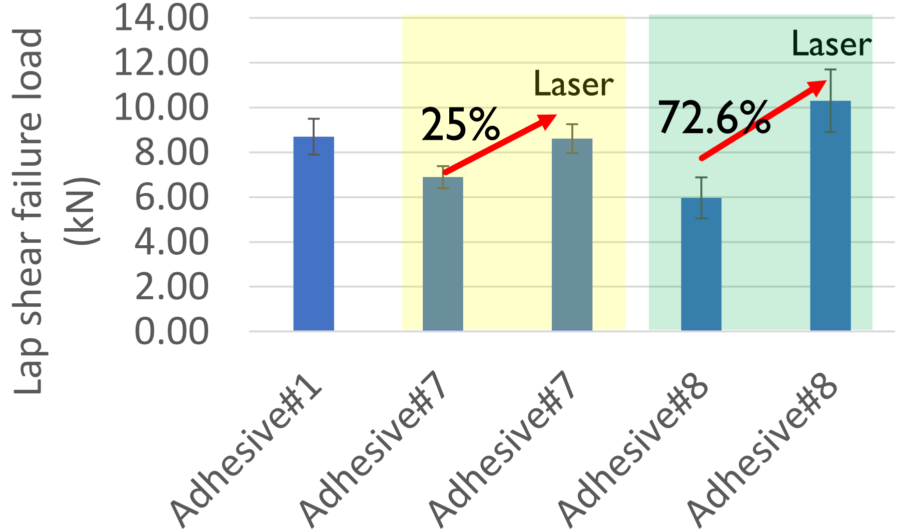
Adhesive#8



As-received CFRP (PPA) Laser treated CFRP (PPA)



Laser surface treatment on CFRP(PPA) shows improved adhesive bonding strength



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RESPONSES TO PREVIOUS YEARS REVIEWERS' COMMENTS

- *"The technical Accomplishments slides were somewhat disjointed, more like literature survey results, and very preliminary results on large differences in lap shear tests. The reviewer would have preferred to see more adhesives used on the same material combination, though the differences of the same (?) adhesive on the three material combinations is interesting. The reviewer asked if the digital image correlation (DIC) is being used to measure strain or only the qualitative nature of strains."*
- **Response:** With supports from several adhesive manufacturers, adhesives with different modulus were investigated in the second year on the same material combination. The DIC technique was applied to observe for deformation of adhesive with different adherend combinations and strains on the adhesive measured during mechanical testing. Furthermore, special DIC system with loading frame is being developed this year to study the deformation and failure of different regions across the substrates, interfaces, and different regions of adhesives with micro meter level spatial resolution.
- *"It would be nice to see additional industry or academic partners in addition to just the DOE national laboratories. The reviewer did not see any mention of transitions to outside DOE to the automotive industry, for example."*
- **Response:** Interactions with automotive industries ramped up in the second year. For example, in addition to major adhesive companies, one of the auto OEMs provided their adhesives to understand their curing behavior with our system and method. Another OEM was interested in micro DIC measurement to better understand adhesive behavior of their dissimilar joint.

COLLABORATION AND COORDINATION

- An integrated R&D team from ORNL and PNNL and Industry partners
  - Closely coordinated research activities and responsibilities as highlighted in Approach on Slide 5
  - Bi-weekly web meetings between research team members
- Adhesives from major adhesive suppliers: Dow Automotive, L&L Product, 3M, PPG
- BASF for thermoplastic CFRP and United State Steel for advanced high strength steel

Core Research Team Members

- ORNL: Zhili Feng, Amit Naskar, Yong Chae Lim, Jian Chen, Ngoc Nguyen, David Warren, Xin Sun
- PNNL: Kevin Simmons, Leo Fifield, Yongsoon Shin, Wenbin Kuang, Gayaneh Petrossan, Daniel Graff, Jonathan Sutter, Matt Prowant

REMAINING CHALLENGES AND BARRIERS

- Limited fundamental understanding of metal to CFRP adhesive bonding characteristics at nano/micro scales;
  - Effects of surface conditions (morphology, chemistry) of substrates
  - Adhesive chemistry and additives, compatible to both AHSS and CRFP
  - Long-term performance and environmental degradations
  - Inhibition of galvanic corrosion,
  - Compatibility with CTE mismatch

- Lack of scientifically sound, effective approaches to design and engineering high performance adhesives and assembly technologies

PROPOSED FUTURE WORK

- Continue on in-depth understanding on interface bonding, deformation and roles of adhesive properties at nano/micro scales (FY18/19)
  - Connect to macroscopic level joint deformation and failure
- Innovative surface modification technology (FY19)
  - Identify and develop surface modification concept based on above in-depth understanding and interface by design for improved bonding strength.
  - Develop processes that will effectively modify both the interface morphology and interface chemistry
- Adhesives tailored for metal to CFRP bonding (FY19/20)
- Heath monitoring of curing/manufacturing process and structural soundness in service (FY19/20)

Any proposed future work is subject to change based on funding levels

SUMMARY

- This early stage research focuses on the fundamentals of adhesive bonding of CFRP to AHSS material combination. In concert with the Interface by Design effort, innovative adhesive bonding concepts would be identified and explored.
- Completed baseline study on the influence of adhesives on bonding strength and failure modes
- Initiated in-depth study on interface bonding, deformation and roles of adhesive properties at nano/micro scales
- Adhesive bonding interface was studied by advanced electron microscopy and nano-indentation
- Surface engineering techniques, including mechanical abrasion and laser treatment, were applied on CFRP (PPA), lead to improved adhesive bonding strength

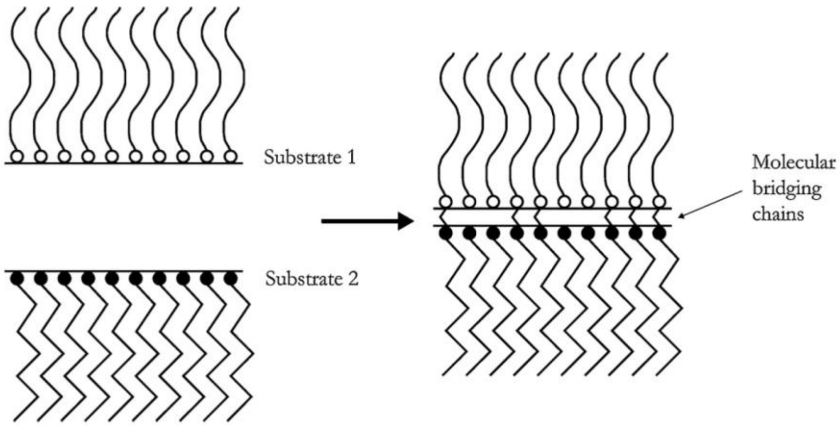
TECHNICAL BACKUP SLIDES

TECHNICAL BACKUP SLIDES

- Up to 5 slides

COMPLEXITY OF ADHESIVE BONDING

- Multi-disciplinary topic
  - surface chemistry
  - Physics
  - Rheology
  - polymer chemistry
  - stress analysis
  - polymer physics
  - fracture analysis
- Adhesion mechanisms
  - Diffusion
  - Mechanical
  - molecular and chemical and thermodynamic adhesion phenomena



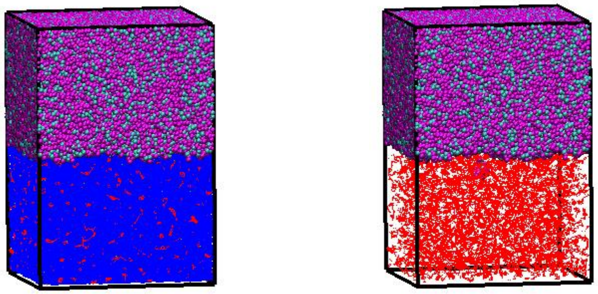
F. Awaja et al. / Progress in Polymer Science 34 (2009) 948–968

MOLECULAR DYNAMIC SIMULATION: CROSSLINKING

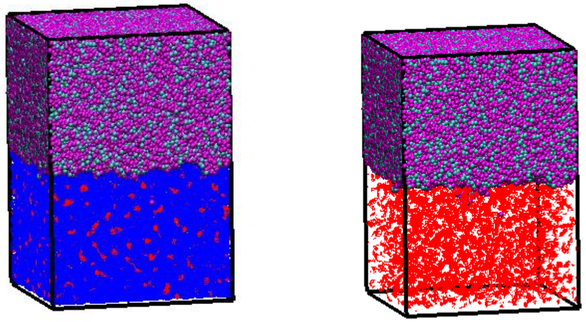
Initial system building

- Box size: 100x100x84 σ
- Epoxy chain length: 81, Number of molecules: 1432
- Nylon chain length: 58, number of monomers: 2000
- Energy Minimization with soft potential
- Box size: 57x57x84
- Total number of monomers: 231999.
- Epoxy crosslinking monomers: 15752
- Density: 0.85 (Melt density)

Magenta and Cyan: Nylon nonpolar and polar monomers
Blue and Torquoise: Epoxy nonpolar and bond-forming polar monomers



SCHEME 1: 98.4% Epoxy crosslinked in 1 million time-steps



SCHEME 2: 98.4% Epoxy crosslinked in 1 million time-steps

Crosslinking is done in 2 ways

- ❖ **SCHEME 1**: Epoxy and Nylon do not interact with each other during crosslinking
- ❖ **SCHEME 2**: Epoxy and Nylon interact favorably (attractive) during crosslinking

Crosslinking scheme:

1. Two bond-forming monomers come within 1.3σ distance.
2. Probability of forming a bond between these two monomers = 0.1
3. The maximum number of bonds the can form is 2. As the monomers are part of epoxy chain, there exists one bond. So, another bond-forming monomer can attach to the crosslinking process

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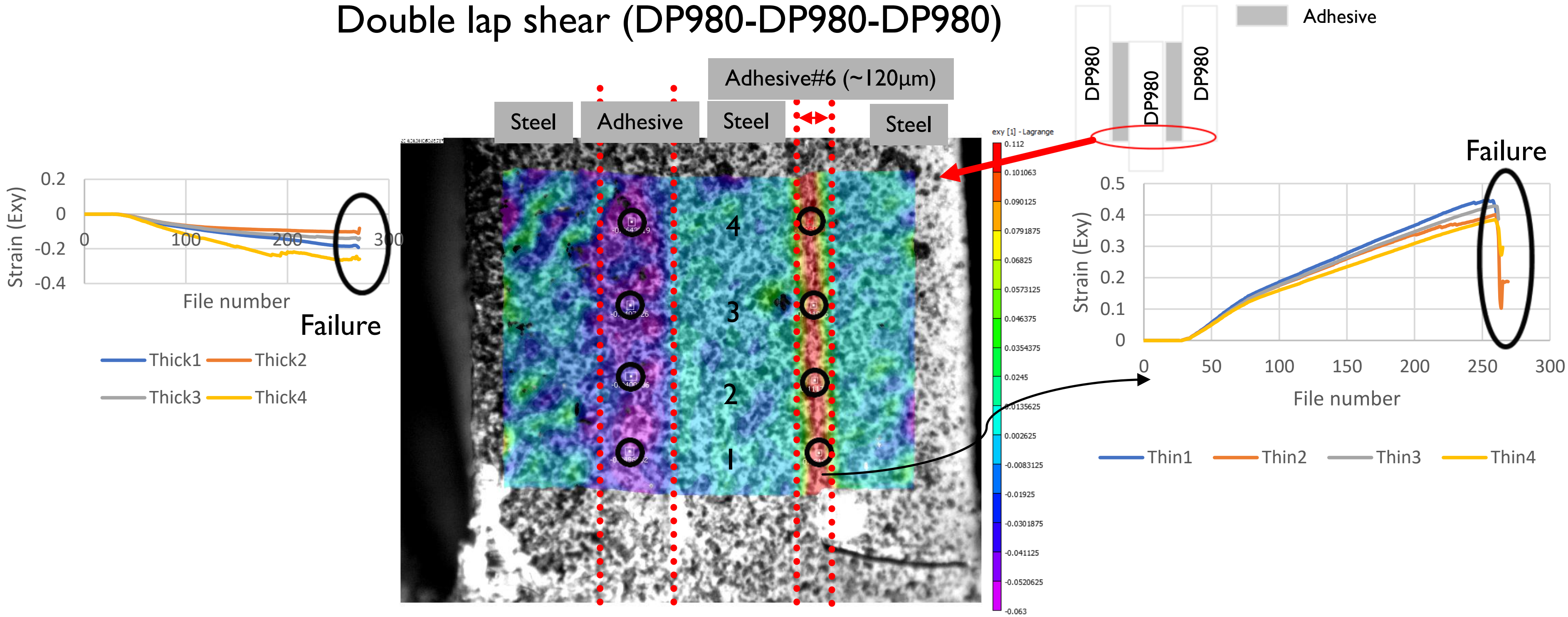
ACCOMPLISHMENTS AND PROGRESS

STRAIN MEASUREMENT FROM DIC TECHNIQUE

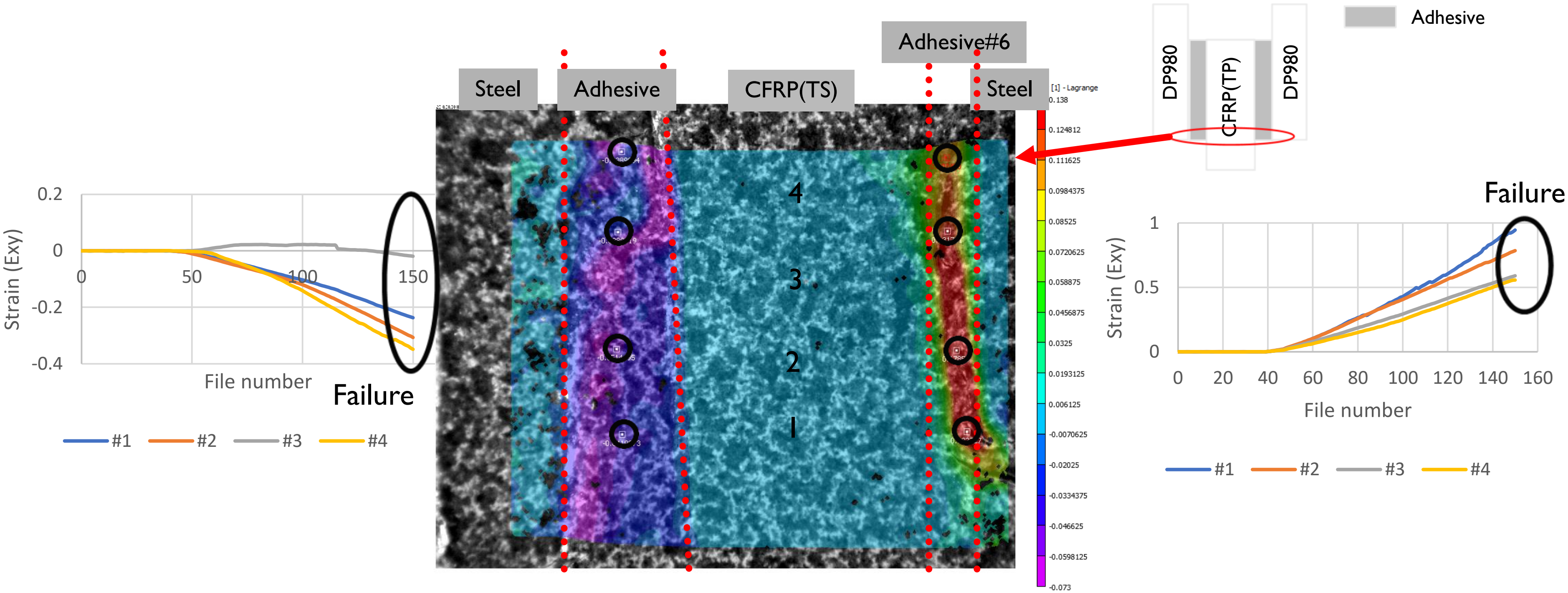
Double lap shear (DP980-DP980-DP980)



- Strain at different locations (1,2,3,4) in adhesive layers was progressively increased until failure
- Strain at relatively thick adhesive layer (left) is lower than the strain at thin adhesive layer (right)

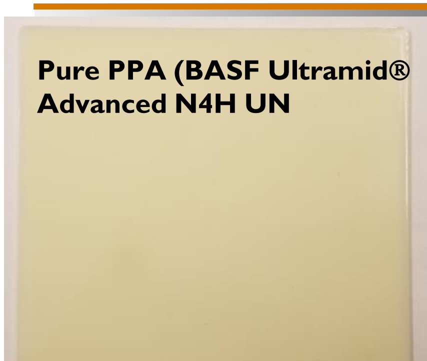
STRAIN MEASUREMENT FROM DIC TECHNIQUE

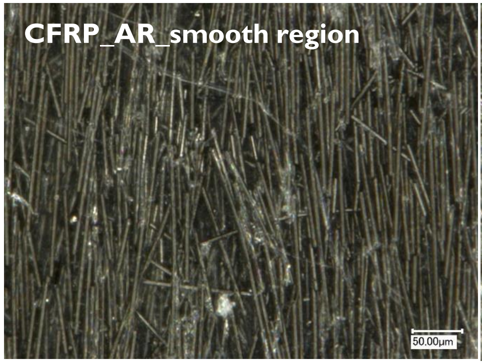
Double lap shear (DP980-CFRP(TS)-DP980)

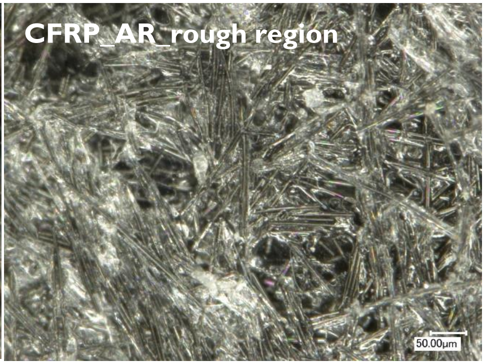


- Strain at different locations (1,2,3,4) in adhesive layers was progressively increased until failure

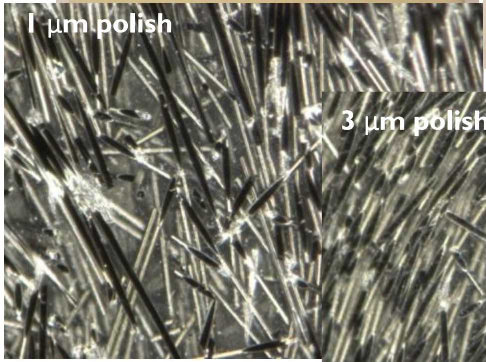
MECHANICAL ABRADING EFFECTS ON WETTING

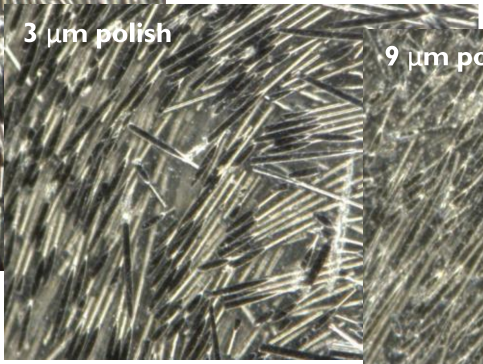


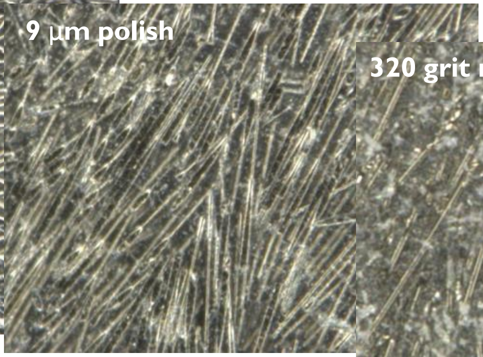


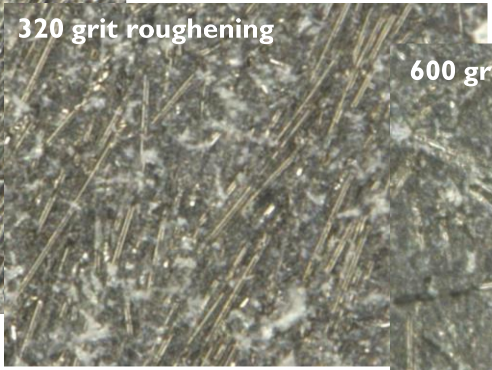


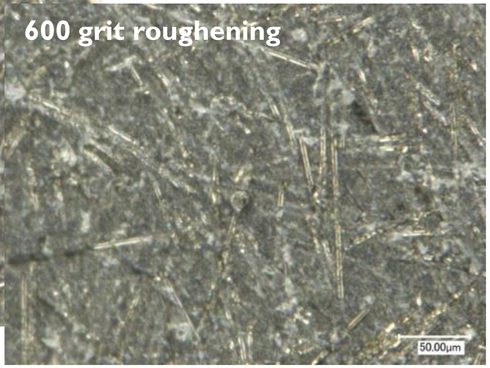
Controlled Surface Modifications











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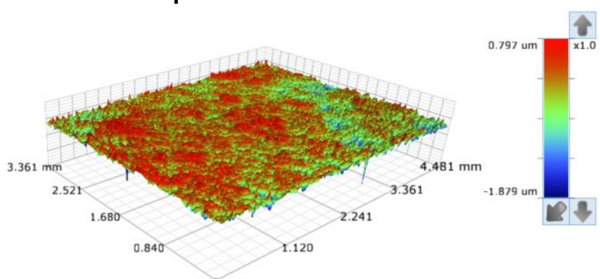
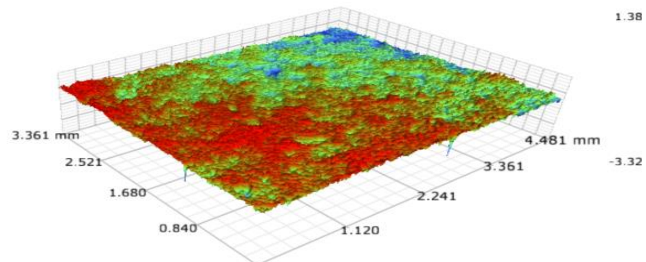
LASER PROFILOMETRY OF DIFFERENT MODIFIED SURFACE TOPOLOGY

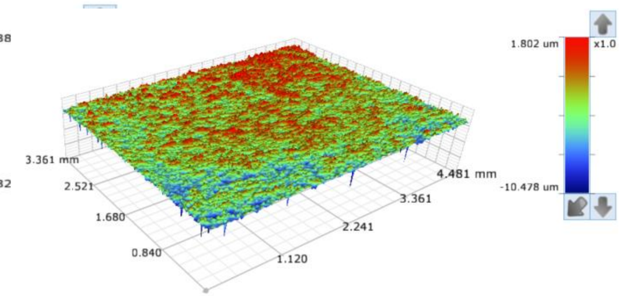
X-1μ-2-3



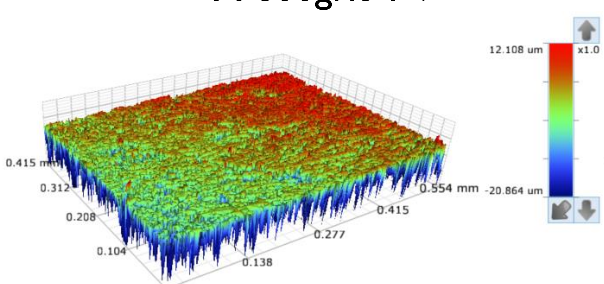
X-3μ-3-1



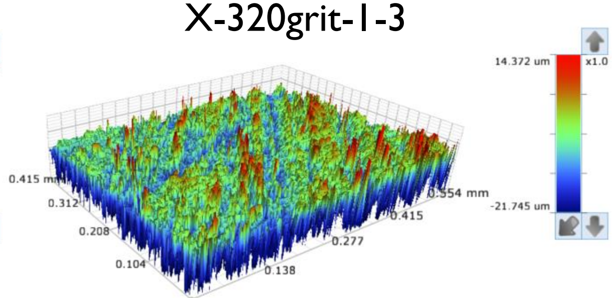
X-9μ-2-5



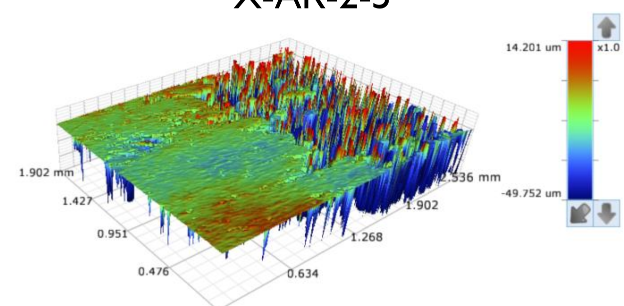
X-600grit-1-9



X-320grit-1-3



X-AR-2-5



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